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Tight-binding surface correction to the embedded-atom method embedding function

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Abstract. The embedded-atom method (EAM) has been highly successful in predicting many properties of fcc metals. However, it is known to underestimate surface energies by as much as 40 to 50%. This suggests that it would be interesting to explore the possibility of obtaining a surface correction to the embedding energy. In this paper, the functional form for a surface embedding function, $F_{surface}$, for the embedded-atom method (EAM) is proposed. The existence of a different F for surface atoms than for bulk atoms stems from the fact that the presence of a surface modifies the energy band structure of the solid. In order to study this change, we used the tight-binding method, that provides the ingredients needed to obtain an explicit expression for the relevant quantities. By comparing the energies of the EAM and tight binding for a surface-terminated bulk, we obtain a correction to the EAM embedding function and the EAM energy for the system. In order to quantify our result we apply it to the lower-index surface planes of Ag and Pd by adjusting our tight-binding parameters with known, available first-principles results for the (111) plane. We then predict the surface energies for the (100) and (110) planes with our method and show an improvement over using the bulk embedding function as compared with first-principles values.

1. Introduction

The embedded-atom method (EAM) has been a very successful semi-empirical method for predicting a variety of properties of fcc metals, such as defects, impurities and phonon spectra [1–7]. However, although predicting physical trends properly, the method gives poorer quantitative results for surface energies. The EAM and similarly constructed methods, such as the Finnis–Sinclair method, seem to underestimate surface energies by as much as 40–50% as compared to experiment and *ab initio* calculations [8–10].

Recently, Haftel [9] has examined this question by guessing a surface embedding function. Other attempts have been made to improve EAM by including higher-order moments [11]. We use the tight-binding method (TB) on a surface in order to obtain the functional for a correction to the embedding energy. In the EAM the electron density used in the evaluation of the embedding energy is constructed by simple overlap of atomic densities. Part of the power of the method results from the simplicity of this approximation. With this in mind, we stay within the original spirit of the EAM by expressing the correction to the embedding energy as a function of the electron density, our hope being that the functional form obtained will prove to have a more general applicability.

The summary of this paper is as follows: in section 2, we obtain the energy band for a bulk-surface system within the tight-binding (TB) framework. In section 3 we give the expressions used for the TB Coulomb and resonance integrals as a function of the near-neighbour distance between atoms. In section 4 we obtain an analytical form for the correction term, due to the presence of the surface, to the bulk EAM embedding function. Once this is accomplished, we use the analytical form of the EAM provided by Johnson [12, 13] to implement calculations. By calibrating our results with those of Methfessel *et al* [8] for (111) planes, in order to fix the unknown TB parameters, we obtain the values of the surface energies for the (100) and (110) surfaces of Ag and Pd.

2. Energy spectrum

In order to define a surface contribution to the embedding energy we consider a cubic crystal and use its band structure within the tight-binding method. The energies in a band are given by:

$$E = \alpha + 2\beta(\cos\theta_1 + \cos\theta_2 + \cos\theta_3) \quad (1)$$

where α is the Coulomb integral and β is the resonance integral. The variables θ_1 , θ_2 and θ_3 are dimensionless reciprocal space coordinates. In the case of a bulk extending indefinitely in all three spatial directions, each of these coordinates exists in the region $[-\pi, \pi]$ at intervals of $2\pi/N$, where N is the linear dimension of the solid under consideration. If, instead, the bulk is terminated at certain plane perpendicular to the z -axis, then θ_3 should be a root of the following equation [14]:

$$z + \cos\theta_3 + \sin\theta_3 \cot(N\theta_3) = 0 \quad (2)$$

where the parameter z is the difference between the bulk and surface Coulomb integrals in units of β : $z = (\alpha - \alpha')/\beta$, where α' is the surface Coulomb integral. If we solve equation (2), and substitute its roots into equation (1), we would find the energy spectrum of a system consisting of a surface-terminated bulk. Equation (2) does not have an analytical solution in the general case. However, by assuming that the difference $\alpha - \alpha'$ is small, we can solve equation (2) by perturbation techniques.

Let us explicitly write

$$\theta_3 = \theta_3^0 + \xi \quad (3)$$

where ξ is a small quantity and θ_3^0 are the roots of equation (2) when $z = 0$:

$$\theta_3 = \frac{\pi}{N+1}s \quad s = 0, 1, 2, \dots, N. \quad (4)$$

If we substitute θ_3 from equation (3) into equation (2), keeping only terms up to first order in ξ , we obtain

$$z + \left[-\sin\theta_3^0 - \frac{N}{\sin(N\theta_3^0)} + \frac{\cos^2\theta_3^0}{\sin\theta_3^0} \right] \xi = 0. \quad (5)$$

Thus,

$$\xi = \frac{z}{\left[\sin\theta_3^0 + \frac{N}{\sin(N\theta_3^0)} - \frac{\cos^2\theta_3^0}{\sin\theta_3^0} \right]}. \quad (6)$$

Equation (1) written in first order in ξ reads

$$E = \alpha + 2\beta(\cos\theta_1 + \cos\theta_2 + \cos\theta_3^0) - 2\beta\xi \sin\theta_3^0. \quad (7)$$

Substitution of ξ from equation (6) into equation (7) provides the energy spectrum of the bulk-surface system. The first term on the right-hand side of the equation is the typical bulk energy term. The second term is the contribution to the energy due to the presence of the surface and will be termed $E_{surface}$.

3. TB versus lattice parameters

In a crystal lattice, the interatomic distance is directly related to its density. To evaluate the EAM density term, we first proceed to evaluate the TB parameters as a function of the interatomic separation, R . From the interaction between two atoms [15, 16], we can write, for the resonance and Coulomb integrals:

$$\beta = P(R) e^{-2\eta R} \tag{8}$$

$$\alpha = E_0 - q \frac{(2\eta)^{2n-1}}{(2n)!} R^{2n-2} e^{-2\eta R} \tag{9}$$

where η is the decay length of an atomic wave function, n is the principal quantum number for the highest occupied atomic level, and $P(R)$ is a polynomial in R .

The TB Coulomb integrals can be rewritten as follows:

$$\alpha = \alpha_0 - \alpha_1 R^{2n-2} e^{-\gamma R} \tag{10}$$

$$\alpha' = \alpha_0 - \alpha'_1 R^{2n-2} e^{-\gamma R} \tag{11}$$

where α_0 , α'_1 and γ are constants that depend on the particular material. In principle they can be evaluated from the higher occupied atomic level, the Fermi energy, the function and the ionization potential. In these expressions, the exponential term corresponds to the effect of the rest of the atoms on the particular integral: the Coulomb integrals go to a constant and the resonance integral tends to zero as the distance between the atoms increases. Notice that α_0 was chosen to be the same for both surface and bulk Coulomb integrals, since at infinite separation, the surface and bulk atoms are indistinguishable, and, in fact, α_0 is the energy of the free-atom state from which the crystal band is built.

4. The EAM surface term

Our purpose in this section is to obtain a functional form for a correction to the embedding energy from the results of sections 2 and 3.

Substituting the results of the previous section into equation (7) and integrating for all states below the Fermi energy,

$$E_{surface} = 2(\alpha_1 - \alpha'_1) R^{2n-2} e^{-2\gamma R} \int_{E < E_F} \left[(d\theta \sin \theta_3^0) / \left(\sin \theta_3^0 + \frac{N}{\sin(N\theta_3^0)} - \frac{\cos^2 \theta_3^0}{\sin \theta_3^0} \right) \right]. \tag{12}$$

We denote the integral up to E_F by I . In the case of metals, it can be calculated explicitly and is

$$I = \frac{\pi}{3} N^2. \tag{13}$$

$E_{surface}$ takes the simple form:

$$E_{surface} = 2I(\alpha_1 - \alpha'_1) R^{2n-2} e^{-\gamma R} \tag{14}$$

On the other hand, the energy can be calculated from the EAM by first considering all N^3 atoms as being bulk and then correcting for the N^2 surface atoms thus

$$E_{EAM} = E_{Bulk} - N^2 F_{Bulk}(\rho_s) + N^2 F_{Surface}(\rho_s) \quad (15)$$

where $F_{Bulk}(\rho_s)$ is the standard embedding function in the EAM obtained from bulk behaviour and $F_{Surface}(\rho_s)$ is the correction proposed from the present method, where ρ_s is the electron density obtained by the regular EAM approach, i.e. superposition of atomic densities.

Now we can identify the EAM energy with the energy of the previously calculated surface-bulk system and get

$$F_{Surface}(\rho_s) = F_{Bulk}(\rho_s) + \frac{2I}{N^2} \frac{\alpha_1}{N_B} (N_B - N_{hkl}) R^{2n-2} e^{-\gamma R} \quad (16)$$

or

$$F_{Surface}(\rho_s) = F_{Bulk}(\rho_s) + \frac{2I}{N^2} \frac{\alpha_1}{N_B} (N_B - N_{hkl}) R^{2n-2} e^{-\gamma R} \quad (17)$$

which defines a functional form for a correction to the embedding energy. In the previous expression, N_{hkl} is the number of nearest neighbours for an (hkl) surface atom and N_B is the number of nearest neighbours for a bulk atom. This is the main result of this work and provides an explicit functional form for a correction to the embedding function in terms of R and which maintains the simplicity of EAM.

For consistency, we need to express the interatomic distance, R , in terms of the surface charge density. This can be done once an electron wave function around the atoms has been chosen. As an example, if we choose hydrogenic ns functions, and consider up to first nearest neighbours,

$$\rho_s = N_{hkl} \frac{\gamma^{2n+1}}{4\pi(2n)!} R^{2n-2} e^{-2\gamma R}. \quad (18)$$

This suggests, from equations (17) and (18), that the correction term can be written as

$$\Delta F(\rho_{Surface}) = \text{constant}(N_{Bulk} - N_{hkl}) \frac{\rho_s}{N_{hkl}}. \quad (19)$$

5. Application to Ag and Pd surfaces

We now test equation (17) by use of Johnson's [12, 13] analytic EAM which provides a simple method for calculating surface energies. Johnson limits the contribution to nearest-neighbour interactions and models the electron density and the pair-repulsion term by exponentials, thus giving a simple, analytic expression for the embedding energy and the pair repulsion in terms of the electron density. The standard, bulk embedding energy is given by

$$F_{Bulk}(\rho) = E_c \left[1 - \frac{\delta}{\omega} \ln \left(\frac{\rho}{\rho_e} \right) \right] \left(\frac{\rho}{\rho_e} \right)^{\delta/\omega} - \Phi_e \left(\frac{\rho}{\rho_e} \right)^{\lambda/\omega} \quad (20)$$

where the density is given by

$$\rho(r) = \rho_e e^{-\omega((r/r_e)-1)} \quad r \leq r_e \quad (21)$$

and the pair repulsion energy is given by

$$\Phi(r) = \Phi_e e^{-\lambda((r/r_e)-1)} \quad r \leq r_e \quad (22)$$

where $\delta = 3(\Omega_e B_e/E_c)^{1/2}$, Ω_e and B_e are the equilibrium atomic volume and bulk modulus, E_c is the cohesive energy, r and r_e are the nearest-neighbour and equilibrium nearest-neighbour distances and ρ_e and Φ_e are the equilibrium values of the electron density and pair repulsion energy. ω and λ are parameters given by Johnson. We proceed by writing $F_{surface}(\rho_s)$ in equation (17) selecting $\gamma = \omega$, fix the unknown constant by using the *ab initio* values of Methfessel *et al* [8] for the (111) planes of Ag and Pd and use the same coefficient to predict the surface energies of the (100) and (110) surfaces. In addition, we include a further addition to the result. The assumption that the Coulomb integral is the same as in equation (16) is equivalent to a bond-breaking argument [17]. Methfessel [17] showed that the variation of the bond strength is proportional to the square root of the co-ordination. Therefore we include a correction to α'_1 to reflect this result, namely we assume $\alpha_{1Surface} = (N_{Bulk}/N_{hkl})^{1/2}\alpha_{1Bulk}$ which modifies the second term in equation (19) giving

$$\Delta F(\rho_{surface}) = \text{constant}(N_{Bulk} - N_{hkl}(N_{Bulk}/N_{hkl})^{1/2})(\rho_s/N_{hkl}). \quad (23)$$

The results are presented in table 1. Two values are given for the (110) surfaces since, unlike the (100) and (111) surfaces, the second plane loses a nearest neighbour in creating the surface, and we therefore present the values with and without the full tight-binding correction for these atoms. As can be seen, this simple approach gives a substantial improvement as compared with the first-principles results of Methfessel *et al* [8].

Table 1. Comparison of predicted values of the surface energies of the (100) and (110) surfaces of Ag and Pd with the EAM [7] values and with the *ab initio* values of Methfessel *et al* [8]. The (111) values of [8] are used as the input to fix the constants. The two values for the (110) surfaces include the atom in the second plane as a bulk and as a surface atom, respectively.

Present results (in ergs cm ⁻²)			
Equation (19)	Equation(23)	EAM [7]	1st principles [8]
Pd			
(111) 1640	1640	1220	1640
(100) 1983	2000	1370	1870
(110) (2041) 2146	(2071) 2170	1490	1970
Ag			
(111) 1210	1210	620	1210
(100) 1423	1440	710	1210
(110) (1417) 1526	(1448) 1553	770	1260

6. Discussion

We have proposed a procedure for determining a correction to the surface embedding energy in the EAM by use of the tight-binding method. The functional form for this correction maintains the original simplicity of the EAM. Using first-principle results and Johnson's analytic EAM, we have shown that this approximation has the potential to give a substantial improvement in agreement with first-principle predictions of the surface energies of the (100) and (110) surfaces of Ag and Pd based on the present result (table 1). The same procedure could have been applied to any metal where EAM applies and first-principle, or other, results were available to fix constants. A further issue arises concerning the application of the present result to other surface defects such as steps. Interestingly, the (110) results

suggest an approach with regard to the definition of a surface atom. Simply taking atoms naively defined as surface atoms in terms of the rigid surface for application of the procedure, and using standard EAM for any other atom (i.e. atoms in the second layer in this case), gives only a 5–7% difference over treating both first- and second-layer atoms as surface atoms (the two (110) values in table 1).

We have also included the results for the square root coordination dependence of the bond strength proposed by Methfessel *et al* [17] in table 1. We did not find that the results were substantially changed by this inclusion. However, we took the proportionality constant to be equal to one. Had we included it as an adjustable parameter the results might have been improved, however this would require further input from either first-principle calculations or other sources to fix this parameter.

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